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# Mononuclear Sb(V) Bromide Complexes with 3-Halopyridinium Cations: Synthesis, Structures, and Thermal Stability

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**Abstract**—Mononuclear complexes (3-XPyH)[$SbBr_6$] (X = Cl (**I**), Br (**II**)) are synthesized by the reactions of $Sb_2O_3$, $Br_2$, and 3-XPy in HBr. Compound **I** is characterized by X-ray structure analysis (CIF file CCDC no. 1818602). The crystals of compounds **I** and **II** are isostructural. The thermal stability of the synthesized complexes is studied by thermogravimetry.

*Keywords:* antimony, halide complexes, X-ray structure analysis, thermogravimetry
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## INTRODUCTION

Interest in halide complexes of post and late transition metals is caused by a series of valuable physicochemical properties manifested by these compounds, in particular, segnetoelectric properties [1–3] and photocatalytic activity [4–6]. The possibility of using some of them (as a rule, iodometallates) in photovoltaic devices attracts special attention [7, 8]. Among Group 15 elements, halobismuthates are most studied as demonstrating a remarkable diversity of structural types [9–18]. At the same time, similar antimony complexes are studied to a lower extent.

About 50 years ago Jacobson and coworkers published a series of articles devoted to the investigation of the reactions in a $Sb_2O_3$–HBr–$Br_2$–cation $Br_x$ system [19–24]. It was shown that, depending on the nature of the organic cation, the reaction products can be of various structures and can contain complex anions in which the Sb atoms have different oxidation states (+3, +5, or mixed-valence bromoantimonates). In addition, in several cases, crystal structure contains polybromide fragments bound to the bromoantimonate anions by specific supramolecular contacts Br···Br. Thus, the complexes belonging to six different groups can be formed (three variants of the oxidation state + formation/nonformation of polybromides). Unfortunately, the published works predominantly discuss crystal structures and contain no data on other important physicochemical properties, in particular, on thermal stability of the obtained compounds. More than ten compounds were obtained [19–24]. An analysis of the relevant literature showed that these works were not continued in spite of evident interest from the viewpoint of the coordination chemistry of Sb.

We recently showed [25] that the Sb(V) bromide complexes obtained via the scheme similar to that presented in [19–24] can be used as components of solar cells. Taking into account increased interest in searching for new compounds capable of using in this area, the further study of reactions of the type $Sb_2O_3$ + HBr + $Br_2$ + cation $Br_x$ and also the full characterization of the obtained complexes, in particular, investigation of their stability, seem to be important.

Two new Sb(V) bromide complexes, (3-XPyH)-[$SbBr_6$] (X = Cl(**I**), Br (**II**)), were synthesized and structurally characterized in this work. The crystal structure of compound **I** was determined by X-ray structure analysis. The crystals of compounds **I** and **II** are isostructural, which is confirmed by the data of X-ray diffraction analysis. Thermal decomposition of both compounds was studied by thermogravimetric (TG) analysis.

## EXPERIMENTAL

Compounds **I** and **II** were synthesized in air. Commercial reagents (reagent grade) were used as received. The manipulations with solutions containing $Br_2$ necessarily required precautions.

**Synthesis of I and II**. A weighed sample of $Sb_2O_3$ (50 mg, 0.17 mmol) was dissolved in concentrated HBr (5 mL), and $Br_2$ (50 μL, 1 mmol) in concentrated HBr

(1 mL) and solutions of 3-XPy (33 μL for **I** and 0.34 mmol for **II**) in HBr (3 mL) were added. A cherry-red crystalline precipitate was formed on keeping the mixture for 24 h at 6°C. The yield was 84 (**I**) and 87% (**II**).

| For $C_5H_5NClBr_6Sb$ (**I**) | | | |
|---|---|---|---|
| Anal. calcd., % | C, 8.5 | H, 0.7 | N, 2.0 |
| Found, % | C, 8.5 | H, 0.8 | N, 2.2 |
| For $C_5H_5NBr_7Sb$ (**II**) | | | |
| Anal. calcd., % | C, 8.0 | H, 0.7 | N, 1.9 |
| Found, % | C, 7.9 | H, 0.8 | N, 2.1 |

The TG analysis was carried out in a helium atmosphere using a TG 209 F1 Iris® microthermobalance (NETZSCH). The weighed sample was 10 mg, an $Al_2O_3$ crucible was used, the gas flow rate was 60 mL/min, and the heating rate was 10 deg/min in a range of 20–300°C. The experimental results were processed using the standard Proteus Analysis software [26].

The X-ray diffraction analyses of polycrystals were carried out on a Shimadzu XRD-7000 diffractometer (Cu$K_\alpha$ radiation, Ni filter, 2θ range 5°–50°, increment 0.03°, acquisition time 1 s). Samples for investigation were prepared as follows. Polycrystals were triturated in an agate mortar in presence of heptane, and obtained suspension was deposited on the polished side of a standard quartz cell. After heptane dried, the sample represented a thin smooth layer (thickness ~100 μm).

**X-ray structure analysis.** The structure of complex **I** was determined using a standard procedure on an Xcalibur diffractometer (Agilent Technologies) at 130 K (Mo$K_\alpha$ radiation, $\lambda$ = 0.71073 Å, graphite monochromator). The reflection intensities were measured in the φ scan mode for narrow (0.5°) frames. An absorption correction was applied empirically by the SCALE3 ABSPACK algorithm (CrysAlisPro, Agilent Technologies, version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET)). The structures were decoded by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms (SHELX 2014/7) [27], ShelXle program [28]. The crystallographic data and structure refinement results are presented in Table 1. The crystal structure was solved using the racemic twin approximation with a contribution of the lower component of 0.35. The hydrogen atoms of the cation were refined in geometrically calculated positions.

The coordinates of atoms and other parameters for the structure of compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1818602; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

As mentioned above, reactions in a $[SbBr_6]^{3-}$–$Br_2$–cation $Br_x$ system (the dissolution of $M_2O_3$ (M = Sb(III), Bi(III)) in haloid acids affords monomeric forms of anionic halide complexes) give bromoantimonates of various structures and compositions with Sb in the oxidation state +3 and +5 or mixed-valence compounds. The complexes of the $A[Sb^VBr_6]$ type (to which compounds **I** and **II** belong) were obtained for A = 1-EtPy$^+$ [25], $Et_4N^+$ [21], and 2-XPyH$^+$ (X = Cl, Br) [29]. The use of other cations based on pyridinium (2-methyl-, 3-methyl-, and 4-methylpyridinium) leads to the formation of compounds, the anionic moiety of which consists of $[Sb^VBr_6]^-$ and $\{Br_3\}^-$ [23, 24, 30]. Unfortunately, the total number of complexes synthesized via the aforementioned scheme is insufficient for the search for relations between the nature of the cation used in the synthesis and the product. It can only be asserted that the type $A[Sb^VBr_6]$ is among the most frequently accomplished variants. The structure of complex **I** and its crystal packing are shown in Fig. 1.

Attempts to obtain single crystals of complex **II** suitable for complete X-ray structure analysis were unsuccessful, but the data of a preliminary experiment found a close resemblance of the unit cell parameters of compounds **I** and **II**. Based on these data and elemental analysis results corresponding to the formula $A[Sb^VBr_6]$, compounds **I** and **II** were assumed to be isostructural. The diffraction pattern of sample **II** was completely indexed by the corresponding single crystal data; i.e., the powdered sample is single-phase. The experimental diffraction pattern of compound **II** in comparison with the theoretical one calculated from the single-crystal data of complex **I** is shown in Fig. 2. The insignificant differences in the peak positions and intensities are caused by different temperatures of the powder and single-crystal experiments and by the effect of the predominant orientation of crystallites.

Compounds **I** and **II** demonstrate unusually high thermal stability for this class of compounds. In both cases, their decomposition starts above 100°C and is accompanied by the mass loss corresponding to the $Br_2$ fragment (Fig. 3). A similar behavior was observed earlier for $Et_4N[SbBr_6]$ and (1-EtPy)$[SbBr_6]$ [26]. At the same time, thermolysis of the complexes containing cations 2-XPyH$^+$ (X = Cl, Br) proceeds via another mechanism: decoordination of Br$^-$, detachment of H$^+$, and loss of HBr occur in the first step followed by the synchronous evaporation of the formed volatiles and complete mass loss below 190°C. It is most likely that the differences in the behavior of the

**Table 1.** Crystallographic characteristics and experimental diffraction details for compound **I**

| Parameter | Value |
|---|---|
| Empirical formula | $C_5H_5NClBr_6Sb$ |
| *FW* | 715.76 |
| Temperature, K | 130 |
| Crystal system | Orthorhombic |
| Space group | $Pca2_1$ |
| *a*, Å | 16.6414(7) |
| *b*, Å | 7.3471(3) |
| *c*, Å | 24.2543(8) |
| *V*, Å$^3$ | 2965.5(2) |
| *Z* | 8 |
| μ, mm$^{-1}$ | 18.18 |
| Crystal sizes, mm | 0.50 × 0.24 × 0.22 |
| Range of data collection over θ, deg | 3.4–28.9 |
| Ranges of reflection indices | $-15 \leq h \leq 22$, $-7 \leq k \leq 9$, $-30 \leq l \leq 33$ |
| Measured reflections | 13045 |
| Independent reflections | 6253 |
| Reflections with $I > 2\sigma(I)$ | 5056 |
| Number of refined parameters | 254 |
| GOOF | 1.02 |
| $R_1$ (for $\|F\|^2$ (for reflections with $I > 2\sigma(I)$)) | 0.072 |
| $wR_2$ (for $\|F\|^2$ (for all reflections) | 0.196 |
| Residual electron density (max/min), e/Å$^3$ | 3.88/–2.76 |

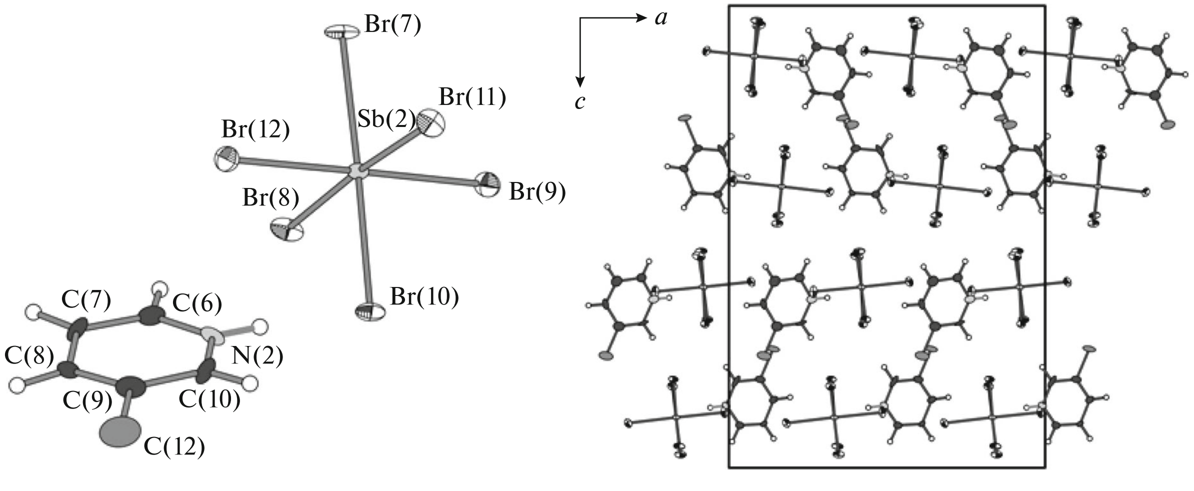


**Fig. 1.** Structure and crystal packing of compound **I**.

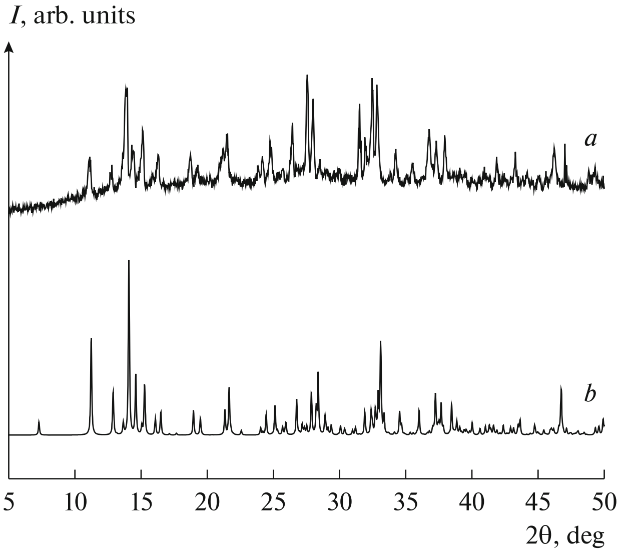
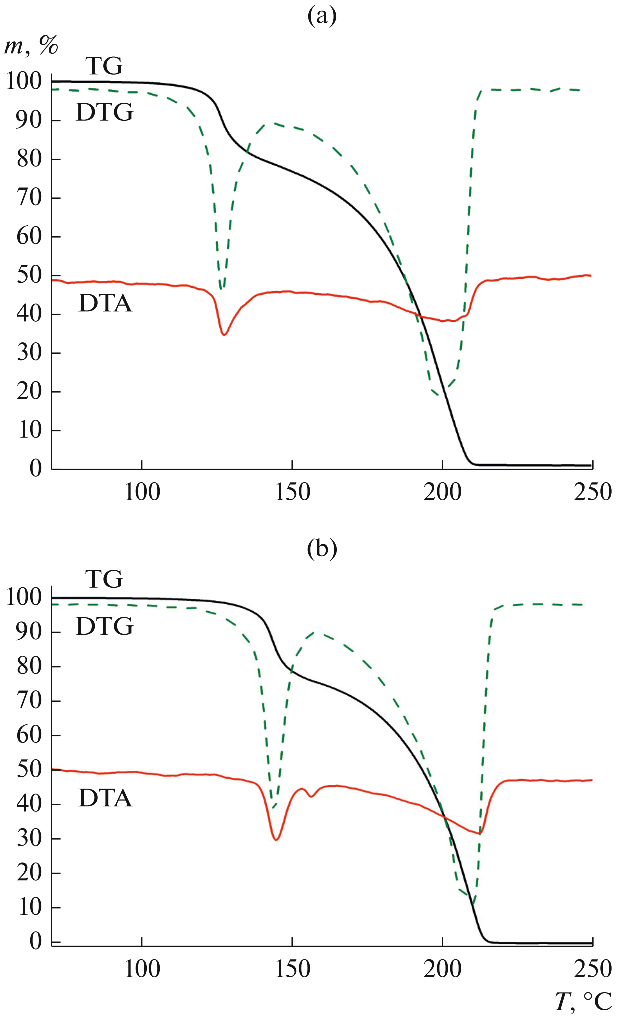


**Fig. 2.** (*a*) Experimental diffraction pattern of compound **II** and (*b*) theoretical diffraction pattern of compound **I**.


(a)

(b)

**Fig. 3.** Thermal analysis curves for compounds (a) **I** and (b) **II**.

complexes containing 2- and 3-halopyridine cations are related to a higher basicity of 3-halopyridines [31].

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